Method Development and Measurements of Polybrominated Diphenyl Ethers (PBDEs) in Tissue, Serum, and Sediment SRMs

Polybrominated diphenyl ethers (PBDEs) are flame retardant compounds that are commonly added to many plastics, resins, and textiles that are then incorporated into products such as TVs, computers, furniture, and carpets. PBDEs can volatilize or leach out of the products in which they are applied and be transported long distances in the environment, due to their physico-chemical properties. Methods have been developed to quantify PBDEs in a variety of Standard Reference Materials (SRMs), and the predominant PBDE congeners have been quantified in marine tissue, human serum, and sediment matrices. The Centers for Disease Control and Prevention (CDC) also provided data for PBDE congeners in the human serum SRM. Data from these methods will be combined to value assign a variety of NIST SRMs for PBDE concentrations.

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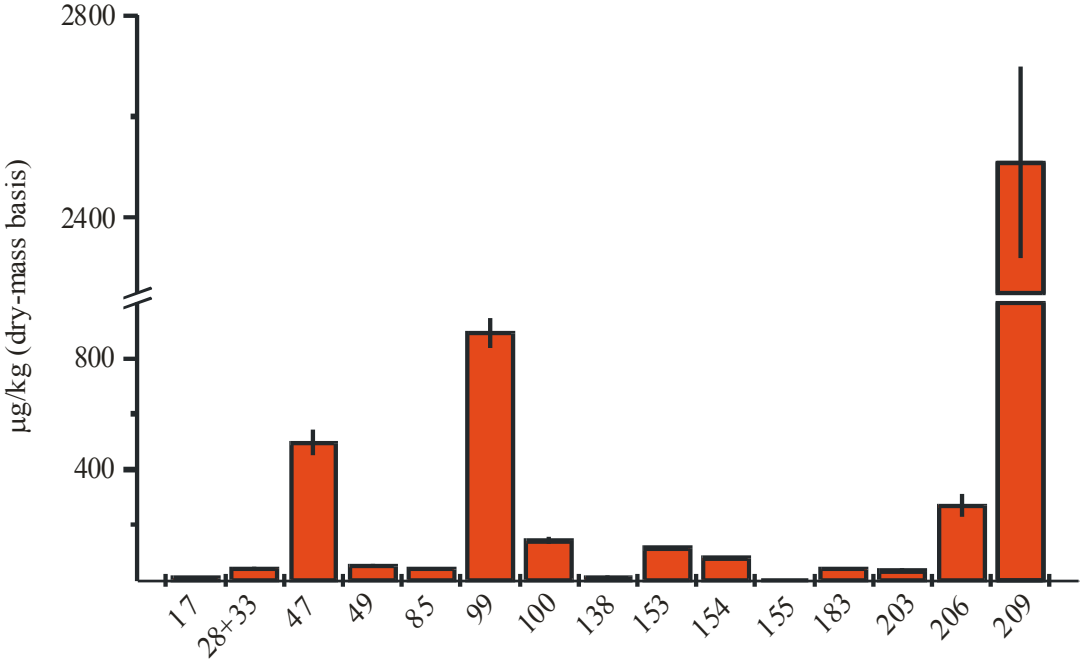
Polybrominated diphenyl ethers (PBDEs) are flame retardant compounds that are commonly added to many plastics, resins, and textiles, and then incorporated into consumer products. PBDEs leach out of these products and are now considered ubiquitous environmental contaminants. Much attention has been focused on their transport, uptake, and fate in both the environment and in humans. Presently, there is an increased need for measurements of PBDEs in environmental matrices and human serum. Reference materials certified for PBDEs are needed to ensure the quality of these measurements.

Ten SRMs have been characterized for a suite of 26 PBDE congeners using highly selective mass spectrometric methods operated in both the electron impact and the negative chemical ionization modes. These SRMs include matrices such as marine mammal tissue, fish tissue, mussel tissue, human serum, marine sediment, and house dust. The development of gas chromatographic methods using cool on-column injection and appropriate capillary columns has allowed for the measurement of the fully brominated PBDE (2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether; BDE 209) using an isotopically labeled PBDE 209 in these materials. This congener has often been difficult to measure due to its thermal instability and its degradation at elevated temperatures. BDE 209 was observed to be the dominant PBDE congener in the sediment and house dust SRMs (see Figure), and thus, these SRMs will be very useful for laboratories interested in routine measurements for BDE 209.

Legislation is now being considered to reduce the use of PBDEs in consumer products. Numerous corporations that produce PBDE-laden products will be affected. These producers will need SRMs characterized for PBDEs to ensure regulatory compliance.



Certified concentrations of selected PBDE congeners in SRM 2585 Organic Contaminants in House Dust. Concentrations range from (3.94 ± 0.34) µg/kg for PBDE congener 155 (2,2',4,4',6,6'-hexabromodiphenyl ether) to (2510 ± 190) µg/kg for PBDE congener 209 (decabromodiphenyl ether

Future Plans:
Projects are being considered to measure other similar analytes in these SRMs. Other flame retardants such as hexabromocyclododecane (HBCD) are now being used at higher rates as a replacement for PBDEs in some parts of the world. Therefore, there is interest in the determination of the concentrations of HBCD in environmental samples. We have already begun method development for the separation and detection of HBCD isomers in environmental samples making use of liquid chromatography and tandem mass spectrometry. Additionally, evidence suggests that PBDEs may be metabolized by some organisms to hydroxylated and methoxylated derivatives. Selected methoxylated PBDEs (MeOBDEs) have been quantified in marine mammal blubber and cod liver oil SRMs.

Publications:

Stapleton, H. M., Dodder, N. G., Kucklick, J. R., Reddy, C. M., Schantz, M. M., Becker, P. R., Gulland, F., Porter, B. J., and Wise, S. A. ***"Temporal Trends in Anthropogenic and Naturally Produced Brominated Compounds in California Sea Lions (Zalophus californianus), 1993 to 2003,"*** Mar. Poll. Bul. *(in press, corrected proof)*, available online 15 November 2005.

Stapleton, H. M., Dodder, N. G., Offenberg, J. H., Schantz, M. M., and Wise, S. A., ***"Polybrominated Diphenyl Ethers in House Dust and Clothes Dryer Lint,"*** Environ. Sci. Technol., 39, 925-931 (2005).

Stapleton, H. M., Harner, T., Shoeib, M., Keller, J. M., Schantz, M. M., Leigh, S. D., and Wise, S. A. ***"Determination of Polybrominated Diphenyl Ethers in Indoor Dust Standard Reference Materials,"*** Anal. Bioanal. Chem. 384:791-800 (2006)

Stapleton, H.M., Keller, J.M., Schantz, M.M., Kucklick, J.R., and Wise, S.A., "**NIST Intercomparison Exercise Program for Polybrominated Diphenyl Ethers (PBDEs) in Marine Sediment: Description and Results of the 2004 Intercomparison Exercise**," NISTIR 7278, NIST, Gaithersburg MD (2006)